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# Anionic PPV polymerization from the sulfinyl precursor route: Block copolymer formation from sequential addition of monomers

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ABSTRACT

The sulfinyl precursor route for the synthesis of poly(*p*-phenylene vinylene) (PPV) materials via an anionic polymerization procedure employing dedicated initiators is evaluated in depth. Reaction kinetics are investigated to gain more control over the polymerization, since polymerization proceeds to full conversion already on the timescale of mixing of the reaction components. Even at −78 °C almost full conversion of the monomer is observed after few seconds. BEH-PPVs are obtained in the range of 3000 to 16,000 g mol$^{-1}$, whereby dispersity decreases with decreasing molecular weight, allowing for materials with a *PDI* of 1.1 for the smallest PPV chain. Block copolymerizations were performed via sequential addition of monomers to make use of the living PPV chain ends. Bimodal product mixtures are obtained, consisting of block copolymer as well as PPV homopolymer. The block copolymer PPV-*b*-poly(*tert*-butyl acrylate) could nevertheless be separated by selective precipitation as well as preparative chromatography techniques.



## 1. Introduction

Poly(*p*-phenylene vinylene)s (PPVs) are one of the most important classes of conjugated polymers studied in polymer science. These materials are applied as donor materials in thin layer devices like organic light emitting diodes and organic photovoltaics [1–4]. While newer classes of low-band gap polymers find nowadays broader application in the realm of photovoltaics [5,6], PPVs remain interesting materials for the simple reason that they can be synthesized to high molecular weights with relative ease on larger scale and – because they are mostly made via chain growth polymerizations – do suffer less from problems associated with upscaling. Many synthesis routes were developed for these materials, from which the so-called precursor routes are the most known and best studied pathways towards soluble and processable PPV materials [7]. For most of these precursor routes a self-initiated free-radical mechanism is observed for which little or no control on molecular weight, endgroups or dispersity could be reached [8–15]. For details on the different synthesis pathways, the reader is referred to a recent review on the matter [7]. To allow for the synthesis of advanced macromolecular structures with sophisticated materials properties, good control over these parameters are, however, required. Defined block or graft copolymers will be only accessible if endgroup and molecular weight control is achieved. Generally, the field of semi-conducting polymers runs behind that of classical polymers with respect to advanced macromolecular design and closing this gap will open up new avenues also outside the classical fields of application of conjugated materials. Different strategies for the synthesis of complex architectures and block copolymers have already been described, for instance via the Wittig reaction, resulting in difficult reaction–deprotection–reaction methods yielding complex oligomers [16,17].

A recent study on the highly selective sulfinyl precursor route [18] in the radical polymerization mode described for the first time that the chain length of PPVs could be controlled when large excesses of the transfer agent $CBr_4$ were employed. The more equivalents $CBr_4$ were used, the lower was the molecular weight of the obtained polymers, following the Mayo equation. Also the chains could be extended with polystyrene (PS) in an ATRP (atom transfer radical polymerization) reaction to reach a PPV-*b*-PS block copolymers [19]. Polydispersities of the PPV blocks remained, however on a level of roughly 2 or larger as must be expected for a chain transfer polymerization.

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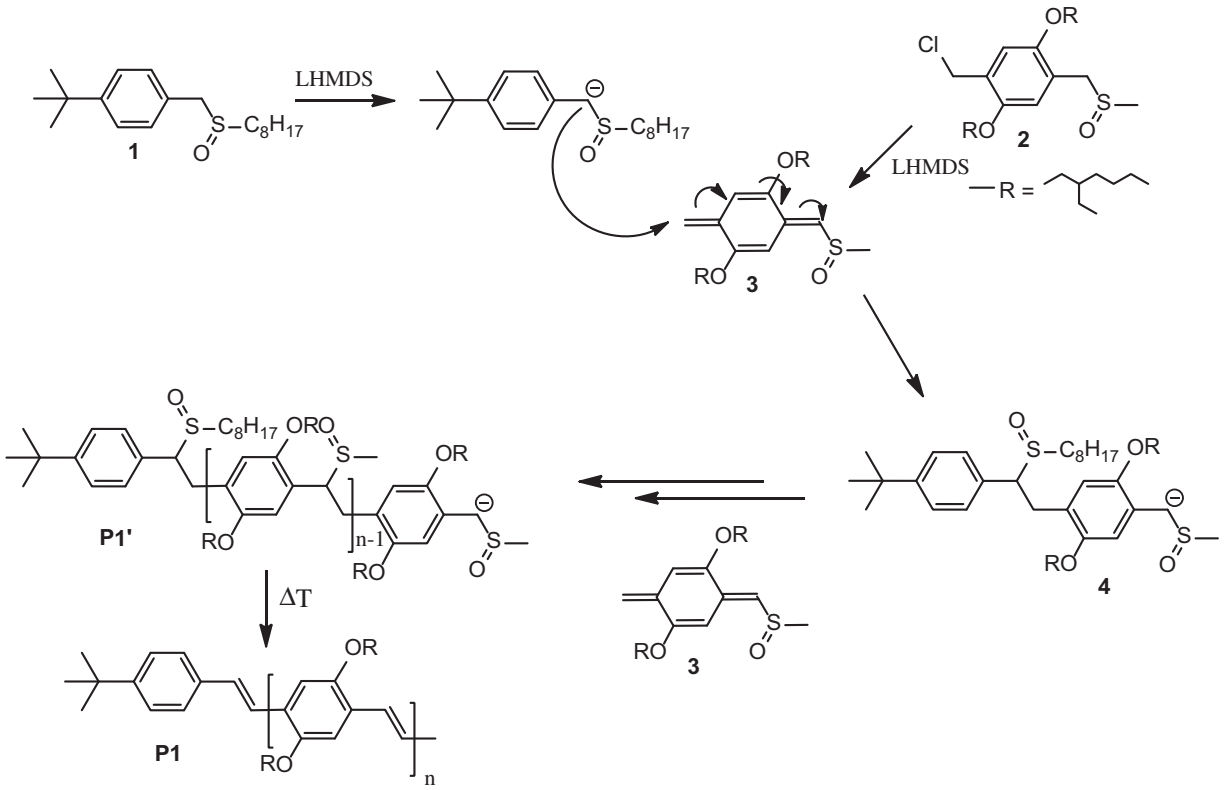
Also, in previous studies, we recently demonstrated that the sulfinyl synthesis route allows for switching between the radical polymerization route and an anionic polymerization mode depending on the choice of solvent and base used to start the reaction (Scheme 1) [20]. In the sulfinyl route, a strong base is generally required to eliminate a leaving group from a precursor monomer to form a polymerizable quinodimethane system (see Scheme 1 for structure). Under most reaction conditions these quinodimethanes are unstable and undergo spontaneous radical polymerization (it should be noted that in older literature very often anionic polymerization conditions were erroneously postulated; newer studies indicate that radical polymerization is much more likely to occur) [9]. To switch from radical to anionic polymerization, the base employed in the in-situ-formation of the actively propagating monomer was changed from *tert*-butoxide to the more sterically hindered base LHMDS (lithium hexamethyldisilazide) while the solvent needs to be replaced by an aprotic solvent such as THF [21].

Anionic polymerization occurs regardless of addition of a dedicated initiator. Product characteristics are, however, greatly improved when dedicated anionic initiators that resemble the monomer in structure are employed as shown in Scheme 1. With such component **1** reasonable control over molecular weight was achieved via varying the concentration of initiator, even if some non-idealities remained. Best results, also in terms of dispersity, were obtained when high initiator concentrations were employed in the synthesis [21]. It is important to note that the anionic PPV polymerization proceeds after a double action of the base LHMDS; the base is required to convert the precursor monomer, but also to deprotonate the initiator. Only after such initiator formation step, a conventional anionic polymerization may occur and a non-conjugated polymer **P1′** is obtained, which can be thermally eliminated to yield the final product **P1**.

In our previous studies we demonstrated that a pure anionic PPV polymerization can be achieved [20,21]. As mentioned above, however, deviations from ideal polymerization were still observed before and doubts remained about the initiation efficiency of the employed initiator. In this contribution we try to elucidate further how efficient the polymerization is with respect to the endgroup functionality in order to find methodologies to utilize the polymerization procedure for block copolymer synthesis and self-assembly of materials. To overcome the difficulties observed before, we focus namely on three aspects of the polymerization:

(i) The anionic polymerizations are extremely fast and polymerizations occur on the timescale of mixing of the individual components (initiator and base). Thus, two different reaction procedures, that is the mode of addition of the initiator and base to the reaction mixture, are investigated. In a further attempt to gain more control over the polymerization reactions, also lower reaction temperatures (−78 °C) were studied at different reaction times to see if better control might be achievable under such conditions. With lowering the temperature and reaction time, kinetics can be influenced and reactions are slowed down. It is expected that lower conversions would be reached at these reaction conditions, allowing for more detailed kinetic investigations.

(ii) A deeper look was taken into the polymerization setup. In collaboration with the University of Groningen where a specialized anionic polymerization setup is available, influences from small impurities on the polymerization was examined. In this paper the results gained with the use of regular Schlenk lines (vacuum/$N_2$, Hasselt technique) are compared to these reached in Groningen on the specialized setup [22,23], which allows to avoid the use of syringes and thus water and/or oxygen intake as much as possible.




**Scheme 1.** Anionic polymerization of BEH-PPV with anionic initiator **1**.

(iii) Finally, also the synthesis of block copolymers by addition of a second monomer to the living PPV polymers is described. Namely *tert*-butyl acrylate (*t*-BuA) was used as the second monomer during the synthesis of the block copolymer. As we will demonstrate, the high reactivity of the living PPV chain ends make block copolymers very challenging, but not entirely impossible. Block copolymers can indeed be made if remaining homopolymers are removed via selective precipitation and advanced chromatography techniques. It should be noted that of course such approach is not the most desirable, but may, however, yield interesting materials. Preparative chromatography is frequently applied for semi-conducting polymer materials and hence employment of such technique displays no major obstacle.

## 2. Experimental section

### 2.1. Materials

All solvents and reagents were purchased from Acros or Aldrich and were used without further purification. THF was dried on an MB-SPS 800 system. On the specialized setup, THF was dried over *tert*-butyl lithium (1.9 M in pentane) and condensed under reduced pressure. *Tert*-butyl acrylate was dried over calcium hydride, distilled under reduced pressure and stored under nitrogen at 6 °C.

### 2.2. Analysis

$^1$H NMR spectra were recorded in $CDCl_3$ on a Varian Inova 300 spectrometer at 300 MHz using a 5 mm probe. FT-IR spectra were collected with a Perkin–Elmer Spectrum One FT-IR spectrophotometer (nominal resolution 4 $cm^{-1}$). Analysis of the MWDs of the polymer samples were performed on a Tosoh EcoSEC System, comprising an autosampler, a PSS guard column SDV (50 × 7.5 mm), followed by three PSS SDV analytical linear XL columns (5 μm, 300 × 7.5 mm) and a differential refractive index detector (Tosoh EcoSEC RI) using tetrahydrofuran (THF) as the eluent at 40 °C with a flow rate of 1 mL $min^{-1}$. The SEC system was calibrated using linear narrow polystyrene standards ranging from 474 to 7.5 × $10^6$ g $mol^{-1}$ (PS ($K = 14.1 \times 10^{-5}$ dL $g^{-1}$ and $\alpha = 0.70$)). Polymer concentrations were in the range of 3–5 mg $mL^{-1}$. Mark–Houwink parameters are not available for the polymers under investigation, thus unless indicated otherwise only apparent values based on polystyrene calibration are discussed.

### 2.3. Polymerization

All polymerization and elimination reactions were carried out as described before [21]. The polymerization temperature of −78 °C was reached with an isopropanol/dry ice bath. To obtain low molecular weight materials, 0.5 equivalents of initiator were used. The synthesis of the precursor polymer was quenched after 15 min by addition of 0.2 mL concentrated HCl solution (37%).

### 2.4. Polymer and block copolymer synthesis with high vacuum line anionic polymerization setup

A dried 50 mL flask was degassed by evacuation on a high vacuum system and backfilled with nitrogen. To this flask the monomer (0.5 mmol, 0.23 g) and initiator **1** were added and it was again evacuated and filled with nitrogen. THF was added by direct distillation of the dried THF under reduced pressure and the full mixture was subjected to three freeze–pump–thaw cycles. The concentration is kept around 50 mmol $L^{-1}$ but cannot exactly be controlled in this way. The flask was then cooled to 0 °C and LHMDS (1M in THF, 1.3 equivalents, 0.65 mL) was added using a degassed syringe. The mixture was stirred for 15 min and quenched with concentrated HCl (37%). Work-up was done as earlier reported [21].

For the block copolymer synthesis, the reaction was not quenched with acid, but *tert*-butyl acrylate (5 equivalents, 2.5 mmol, 0.36 mL) was added using a degassed syringe and the reaction was consequently stirred for another 15 min at 0 °C and quenched with methanol. Work-up and elimination was again performed as described before [21]. The conjugated polymer was precipitated in a MeOH/HCl (2/1) mixture and was filtered as a sticky red solid. Afterwards the dried polymer was separated with the use of recycling preparative HPLC.

### 2.5. Separation of polymers

Separation of polymers after selective precipitation were performed on a recycling preparative HPLC LC-9210 NEXT system in the manual injection mode (3 mL) comprising a JAIGEL-2H and JAIGEL-3H column and a NEXT series UV detector using $CHCl_3$ as the eluent with a flow rate of 3.5 mL $min^{-1}$. Fractions were collected manually.

## 3. Results and discussion

### 3.1. Influence of the mode of compound addition and effect of lowering reaction temperature

One of the advantages of anionic polymerizations is that the endgroups of the polymer chains are well-defined. In case of PPV, the use of dedicated anionic initiators leads towards better defined polymer chains concerning molecular weights and polydispersities (PDIs) as described before [21]. An important aspect of PPV polymerization is that the associated reactions are particularly fast, proceeding on the timescale of seconds. Thus, the employed procedure of adding compounds may have a significant influence on the outcome of the polymerization reaction. If the base is added to a mixture of monomer and initiator, then both elimination/deprotonation reactions occur at the same instance. If the initiator is premixed with the base, then chain initiation can in principle start faster and only the monomer precursor elimination is rate-limiting. Therefore, the effect of the addition of initiator **1** [21] to the reaction mixture in different concentrations was investigated by means of two different addition modes. In the first series of experiments (see Fig. 1, red circles, B => M + I), the monomer was mixed with the initiator and dissolved in dry THF. The base (LHMDS (1M solution in THF)) was added directly to this mixture and stirred for 15 min at 0 °C. For the second series of experiments (see Fig. 1, green triangles in web version, I + B => M), the base and initiator were mixed first (in half the amount of solvent) and then added in one batch to the monomer in solution. Again the reaction was stirred for 15 min at 0 °C and work-up was done as described before [21]. Results for molecular weights and PDIs are given in Table 1. It must be noted that only apparent molecular weights $M_n^{app}$ are reported since the polymers were measured on a GPC with conventional polystyrene calibration, which nevertheless allows for qualitative discussion of results and to discern trends. Absolute molecular weights were determined for selected samples via light scattering; those results will be discussed below.

From Table 1 and Fig. 1 it can be concluded that both addition modes show within limits of accuracy the same results regarding molecular weights and polydispersities and no improvement over the reaction could be gained by changing the reaction procedure. At first glance, this result appears to be little surprising. Since monomer formation as well as polymerization take place on the

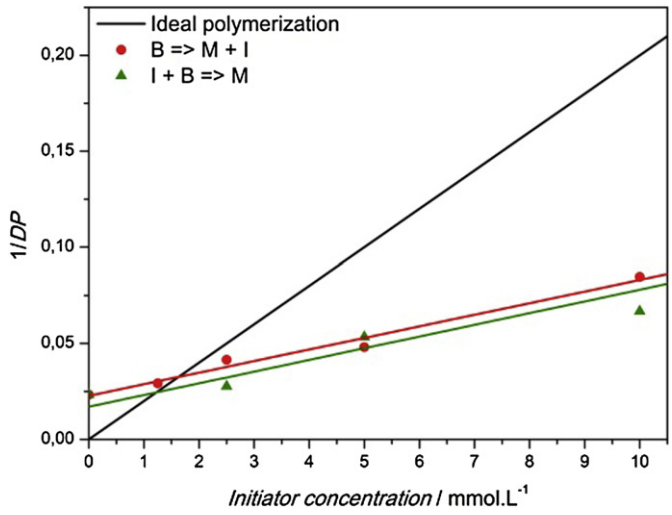



**Fig. 1.** Apparent inverse of the degree of polymerization reached in polymerizations at different initiator concentrations and different addition modes of initiator **1**.

timescale of mixing of the components, differences in the product depending on the practical procedure have been often observed in the past for PPVs [24]. Regardless, for practical reasons this outcome simplifies discussion of further results. It seems, however, to be mandatory to perform such check for each system under investigation.

In order to understand the polymerization mechanism better, the reaction temperature was decreased to slow down the reaction. Therefore, the reaction initiated by 0.1 equivalents of initiator **1** was repeated at −78 °C and polymerizations carried out for 15, 2 and virtually zero minutes reaction time (zero meaning that the reaction was quenched via insertion of an acid solution right after addition of the base). If the reaction could be slowed down in this way, yields and molecular weights should become lower than observed at the usual 0 °C and a progress in molecular weight with time may become observable. The results from these experiments are summarized in Table 2 (addition mode I + B => M).

From the results in Table 2, it is clear that even at −78 °C, the molecular weights and yields are − within some scatter − practically identical compared to for the reactions at 0 °C. No significant difference herein could be found when the reaction time was shortened to 2 min. The only advantage of doing the reaction at lower temperatures is the observed drop in polydispersity. Even if the polymerization reaction is quenched with acid directly after addition of the base ("0" minutes reaction time) at −78 °C, the obtained molecular weight and yield are very high (80%). It can thus be concluded that the anionic polymerization of PPV materials via the sulfinyl precursor route cannot be delayed by means of lowering the temperature and is already finished upon mixing of the components. This also implies that the progression of polymerization in terms of kinetics and molecular weight evolution in

**Table 1**
Results for MW and PDI for the different addition modes and initiator concentrations.

| [In] (mmol $L^{-1}$) | B => M + I | | I + B => M | |
|---|---|---|---|---|
| | $M_n^{app}$ (g $mol^{-1}$) | PDI | $M_n^{app}$ (g $mol^{-1}$) | PDI |
| 0 | 15,600 | 2.4 | 15,600 | 2.4 |
| 1.25 | 12,300 | 2.2 | | |
| 2.5 | 8600 | 2.0 | 13,000 | 2.2 |
| 5 | 7400 | 2.1 | 6700 | 2.1 |
| 10 | 4200 | 1.4 | 5300 | 1.5 |

**Table 2**
Comparison of molecular weights for polymerization reactions at 0 °C and −78 °C.

| Reaction time (min) | 0 °C | | | −78 °C | | |
|---|---|---|---|---|---|---|
| | $M_n^{app}$ (g $mol^{-1}$) | PDI | Yield (%) | $M_n^{app}$ (g $mol^{-1}$) | PDI | Yield (%) |
| 15 | 6700 | 2.1 | 95 | 5900 | 1.5 | 93 |
| 2 | 9700 | 2.0 | 94 | 6000 | 1.5 | 94 |
| "0" | | | | 8100 | 1.9 | 80 |

the anionic polymerization reaction can by practical means not be studied.

### 3.2. Anionic polymerization setup

Because no control could be gained over the anionic polymerization reaction by lowering the reaction temperature to −78 °C, insights were taken into the polymerization setup. All earlier published [20,21] and above described polymers were synthesized via the anionic route using regular Schlenk lines (vacuum/$N_2$). For comparison, experiments using different equivalents of anionic initiator **1** were repeated on a high vacuum line anionic polymerization setup with a high vacuum pump which is available at the University of Groningen. Results for molecular weights and PDIs for the eliminated polymer **P1** are collated in Table 3 and summarized in Fig. 2.

From Table 3 and Fig. 2, it is clear that the same trends regarding molecular weight and polydispersity are observed regardless of the setup used for the synthesis of the polymer. If the initiator concentration is plotted against the inverse of the degree of polymerization, the same linear trend is found. With the use of more equivalents of the dedicated anionic initiator, lower molecular weights and dispersities were gained in both cases. It can thus be concluded that similar results were generated for both setups and that the method, using a conventional Schlenk line to synthesize PPV materials via the anionic pathway, may seem a bit rough at first sight but leads to reproducible and reliable results for the anionic polymerization pathway. If the results of the conventional GPC (measured towards polystyrene standards) are compared to results gained with MALLS (multi angle light scattering) detection, it can be seen that the number average molecular weights are in good agreement for both characterization techniques. This agreement is essentially coincidental, but is of course advantageous since it simplifies further investigations tremendously. When analysing the polydispersities, however, one sees a significant difference. MALLS reveals that the molecular weight distributions are associated with a significantly lower dispersity than they appear to be in conventional GPC. The MALLS data show that for all samples PDI's of <1.5 are obtained, which underpins that the polymerization indeed proceeds via a living polymerization pathway [25]. At the highest initiator concentration, a dispersity of 1.1 is reached, which is an exceptionally narrow distribution for a conjugated polymer material. This observation should not be underestimated. Self-assembly of materials may only become possible when precise and narrow block length distributions are accessible. Via the radical pathway mentioned above, so far only PPV blocks with a dispersity of minimal 2 were obtainable, thus the present data reveal a significant advantage of the anionic polymerization route, that was previously not acknowledged.

### 3.3. Block copolymer synthesis on high vacuum line

By synthesizing the PPVs via the anionic polymerization pathway, a living chain end is created and can be used to synthesize block copolymers by addition of a second monomer to the polymerization mixture. For the synthesis of the PPV-*b*-P(*t*-BuA) block

**Table 3**
Comparison of $M_n$ and PDI for BEH-PPV **P1** synthesized on Schlenk lines or on a high vacuum anionic polymerization setup.

| [In] (mmol $L^{-1}$) | Schlenk lines | | | | High vacuum line | | | |
|---|---|---|---|---|---|---|---|---|
| | Conventional GPC | | MALLS | | Conventional GPC | | MALLS | |
| | $M_n^{app}$ (g $mol^{-1}$) | PDI | $M_n$ (g $mol^{-1}$) | PDI | $M_n^{app}$ (g $mol^{-1}$) | PDI | $M_n$ (g $mol^{-1}$) | PDI |
| 0 | 15,600 | 2.4 | 15,500 | 1.4 | 13,100 | 2.2 | 13,300 | 1.5 |
| 2.5 | 8600 | 2.0 | 9600 | 1.3 | | | | |
| 5 | 7400 | 2.1 | 7800 | 1.3 | 5200 | 1.7 | 6000 | 1.4 |
| 10 | 4200 | 1.4 | 4500 | 1.3 | | | | |
| 15 | | | | | 3400 | 1.3 | 3900 | 1.2 |
| 25 | 2800 | 1.2 | 3000 | 1.1 | 2600 | 1.2 | 3000 | 1.1 |

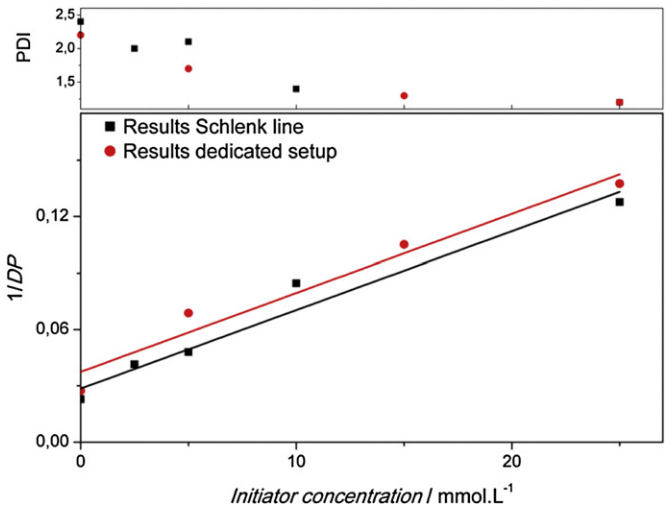
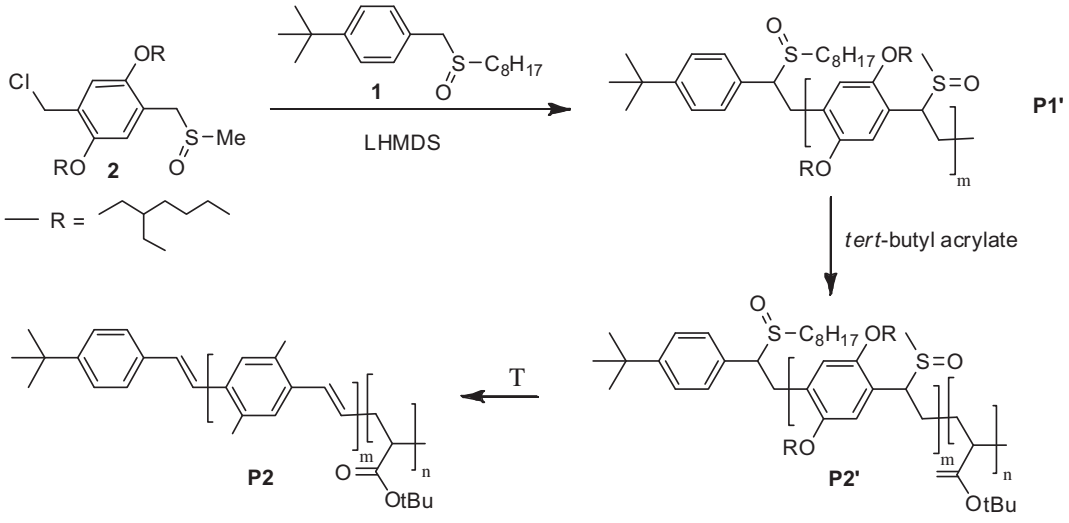



**Fig. 2.** Comparison of apparent $M_n$ and PDI for PPVs synthesized on Schlenk lines (black squares) or with high vacuum line (red circles) measured on conventional GPC. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

copolymer, the same anionic initiator with *tert*-butyl functionality (**1**) is used and polymerized with monomer **2** (Scheme 2). After 15 min of reaction time at 0 °C, 5 equivalents of *tert*-butyl acrylate were added to the reaction mixture and stirred for further 15 min at 0 °C. The polymerization reaction was then quenched with methanol and extracted with $CH_2Cl_2$. After evaporation of the solvent the precursor block copolymer **P2′** was obtained as a sticky yellow solid. After elimination (3 h reflux in toluene), precipitation and filtration, the conjugated polymer **P2** was obtained as a red solid. With the goal to synthesize block copolymers via the living chain end of the PPV block, also styrene was tested as the monomer for sequential polymerization. The same procedure was followed as described above, but no block copolymer could be identified in the product mixture. The reason for the failure of this experiment could not be identified so far and it can only be speculated that the anionic chain end of the PPV precursor polymer chain does not favour styrene addition. In a different attempt to synthesize a block copolymer with a PPV and a polystyrene (PS) block, styrene was polymerized first, initiated by *sec*-BuLi, followed by addition of the sulfinyl monomer **2** after 15 min of reaction time at −78 °C. In this case a bimodal (no addition of LHMDS to the system) or even a trimodal (addition of LHMDS directly after addition of monomer **2**) GPC profile was measured. The different peaks in the chromatogram could essentially be assigned to homopolymers rather than block copolymers. The reason for the failure of also this method lies in the basic nature of the active anionic polystyrene chain ends. These resemble themselves species that can deprotonate the sulfinyl monomer, thus activating the PPV polymerization while concomitantly deactivating the polystyrene chains. Thus, before PPV can be added to the chain ends, all anionic centres have already been quenched.

The only successful method was the first described block extension of the PPV precursor chains with *tert*-butyl acrylate (see Scheme 2). Still, the chromatogram measured for the non-purified precursor polymer **P2′** shows a bimodal molecular weight distribution (see Fig. 3 and Table 4 for MW values), indicating that not all PPV chains were able to react further and form a block copolymer. Thus, the reaction product resembles a mixture of PPV homopolymer and block copolymer (homopolymer of the acrylate cannot be formed, since no other initiator was present to start chain growth).




**Scheme 2.** Synthesis of BEH-PPV-*b*-P(*t*-BuA) block copolymer **P2**.

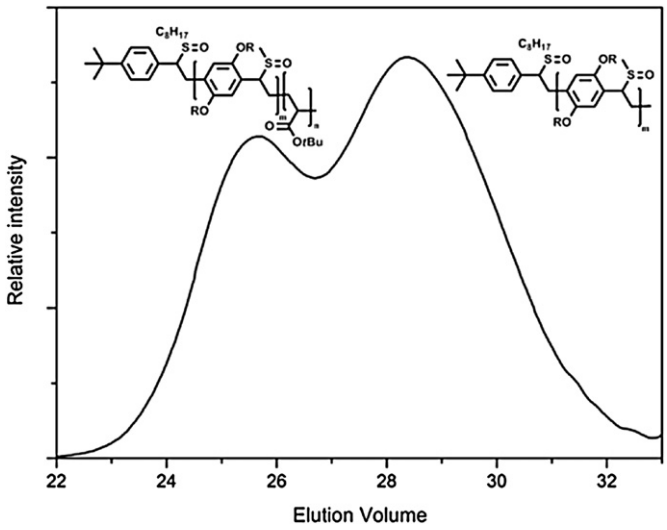



**Fig. 3.** GPC profile for the precursor block copolymer PPV-*b*-P(*t*-BuA) **P2′**.

After elimination of the materials to form the conjugated PPV blocks, copolymer **P2** could not be precipitated in MeOH (the usual non-solvent for PPV materials) but only in a MeOH/HCl (2/1) mixture. This indicates successful chain addition of the acrylate because pure acrylate homopolymer would dissolve in this solvent mixture. After precipitation, again a bimodal GPC profile is observed (Fig. 4 and Table 4), however the bimodality is less pronounced due to the selective precipitation. For comparison, the molecular weights of pure BEH-PPV (synthesised with 0.1 equivalents of anionic initiator **1**) are also collated in Table 4. For the precursor and conjugated PPV polymer, respectively, an apparent molecular weight of 3400 and 5200 g mol$^{-1}$ was found. In this way, it becomes clear that the low molecular weight part (high elution volumes) of the bimodality for **P2′** and **P2** is in agreement with these values. It must be pointed out that the molecular weights, measured by means of GPC towards polystyrene standards, for the rod-coil block copolymers **P2′** and **P2** are only a rough estimation of the real molecular weights because of the difference in hydrodynamic volume for the different polymer blocks. Molecular masses should thus be seen as qualitative rather than quantitative indicators.

**Table 4**
Molecular weights and polydispersities obtained from conventional SEC for block copolymers **P2′** and **P2** and the purified block copolymer fraction of **P2** compared to BEH-PPV.

| | Precursor polymer | | Conjugated polymer | |
|---|---|---|---|---|
| | $M_n^{app}$ (g mol$^{-1}$) | PDI | $M_n^{app}$ (g mol$^{-1}$) | PDI |
| Pure PPV | 3400 | 1.8 | 5200 | 1.7 |
| Before purification | 6600 | 4.7 | 8900 | 3.2 |
| After purification, high MW fraction | | | 48,300 | 1.2 |

To further purify the polymer obtained, the conjugated block copolymer **P2** was subjected to recycling preparative GPC, a standard technique for the separation of conjugated polymer materials [26,27]. In this way, the block copolymer **P2** could be separated from the homopolymer **P1**. The polymers were fractionated during the second cycle (collected from 88.7 to 95.1 min, see Fig. 4).

After fractionation, the high molecular weight fraction was characterized using $^1$H NMR, FT-IR, UV–Vis and fluorescence spectrometry, TGA (thermo gravimetric analysis) and DSC (differential scanning calorimetry) measurements. Spectra can be found in supporting information. From the selective precipitation of the conjugated polymer **P2**, it was already clear that a PPV-*b*-P(*t*-BuA) block copolymer was formed. This is further proven with the use of FT-IR and $^1$H NMR spectroscopy. If the FT-IR spectra for the pure BEH-PPV **P1** (black line, Fig. 5) and BEH-PPV-*b*-P(*t*-BuA) **P2** (red line, Fig. 5) are compared, it is clear that signals at 1728, 1368 and 1150 cm$^{-1}$ appear which can be assigned to the carbonyl functionality of the acrylate block that is now attached to the PPV block.

The $^1$H NMR spectrum for the high molecular weight fraction of **P2** (Supporting information, Fig. S1) also shows signals for both the PPV and the poly(*tert*-butyl acrylate) block. From this NMR spectrum, integrating the signal for the aromatic protons of the PPV main chain, the length of the different blocks of **P2** could be calculated. For the eliminated BEH-PPV, synthesized with the use of 0.1 equivalents of initiator, an average molecular weight of around 5200 is found (see Table 4). This translates to an average of 15 PPV units present in the first polymer block (molecular weight of one unit = 357 g mol$^{-1}$). From the integration of the peak at 2.23 ppm (the signal for the CH group present in the main chain of P(*t*-BuA)), it can thus be concluded that around 250 units of acrylate are

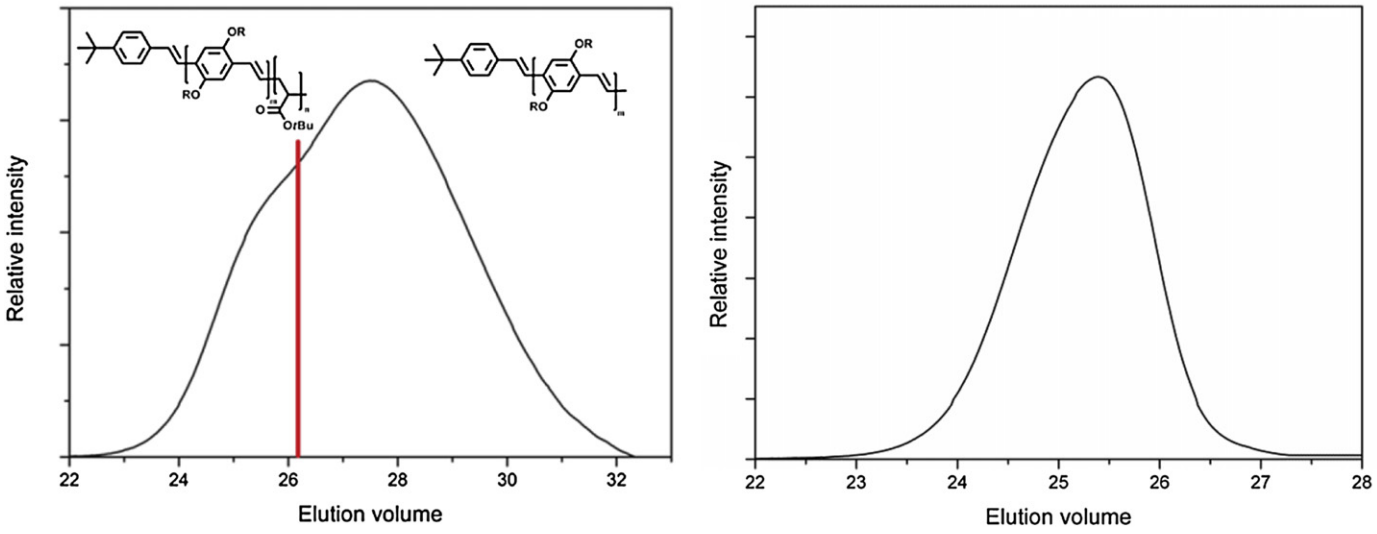



**Fig. 4.** GPC profile for the eliminated PPV-*b*-P(*t*-BuA) **P2** before (left) and separation on recycling HPLC.

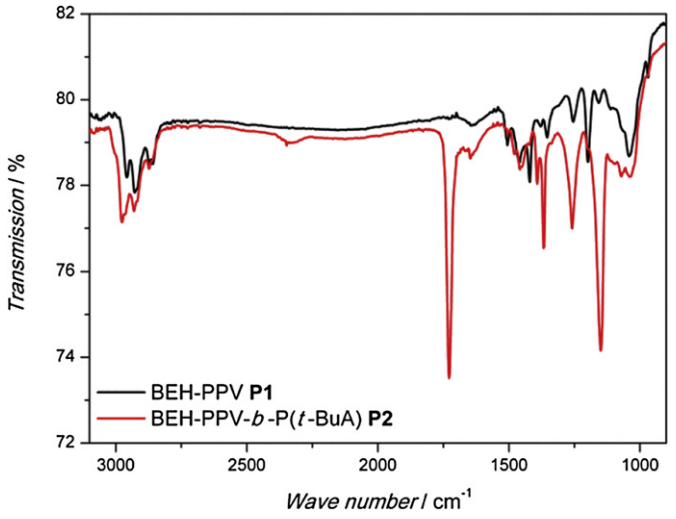



**Fig. 5.** FT-IR spectra for BEH-PPV **P1** (black line) and BEH-PPV-*b*-P(*t*-BuA) **P2** (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

present in the block copolymer. If the total molecular weight is now calculated from this amount of units derived from the NMR spectrum, a total value of 37,200 g mol$^{-1}$ is reached (5200 for the PPV block and 32,000 for the acrylate block). In comparison to these calculated values, the molecular weight determined with conventional GPC (48,300 g mol$^{-1}$) is in good agreement (within the error of measuring the molecular weights of these materials towards polystyrene standards).

In contrast, however, if one would calculate the theoretical amount of acrylate units for full conversion, the molecular weight of the acrylate block should have been around 6400. This mismatch between the theoretically expected composition and the experimentally derived one can be explained by only partial reinitiation of the chains (as already indicated by the bimodality) as well as preparative separation of the polymers, which have cut out systematically lower molecular weight blocks, thus also shifting the average molecular weights.

## 4. Conclusions

In conclusion, PPV formation via the anionic polymerization mode in the sulfinyl precursor route is very fast and yields narrowly distributed PPV materials. Reactions proceed on the timescale of mixing of the components and two different addition modes of components were tested, which gave the same results regarding molecular weights and polydispersities. Even by polymerizing at very low temperatures (−78 °C) no further control could be gained besides a slight improvement in polydispersity. A direct quenching experiment revealed that the polymerization reaction is also at that temperature already finished upon mixing of the different components. If the PPV polymerizations are repeated on a dedicated high vacuum anionic polymerization setup, gained molecular weights and polydispersities are similar. The use of regular Schlenk lines is thus a good synthetic tool to reach reproducible results for the anionic PPV polymerization via the sulfinyl route. For the synthesis of block copolymers, making use of the living chain end of the PPV chain was not fully successful. Formation of block copolymer occurred, but also PPV homopolymer remained in the product mixture. After selective precipitation and fractionation on a preparative recycling GPC, a high molecular weight block copolymer could nevertheless be successful isolated. Block structure and composition were confirmed via FT-IR and $^1$H NMR measurements.

This study marks a significant step towards further investigations in to PPV-containing block copolymer materials. While still essentially successful in the goal of producing block copolymers (at least on small scale), it is clear from the above described investigations that sequential monomer addition is not suitable to prepare block structures efficiently. Future studies will thus focus on the possibility to use functionalized anionic initiators to reach the goal of well-defined endgroup structures (on the chain-initiating side) in the PPV chains, which can then likewise be used to prepare block copolymers.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2012.12.070.

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